Polymers grafted to porous membranes

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We study a single flexible chain molecule grafted to a membrane which has pores of size slightly larger than the monomer size. On both sides of the membrane there is the same solvent. When this solvent is good, i.e. when the polymer is described by a self avoiding walk, it can fairly easily penetrate the membrane, so that the average number of membrane crossings tends, for chain length $N \to \infty$, to a positive constant. The average numbers of monomers on either side of the membrane diverges in this limit, although their ratio becomes infinite. For a poor solvent, in contrast, the entire polymer is located, for large N, on one side of the membrane. For good and for theta solvents (ideal polymers) we find scaling laws, whose exponents can in the latter case be easily understood from the behaviour of random walks.

Long chain polymers in dilute solutions have important technical applications, but they also form an interesting model for studying scaling and renormalization group techniques [1, 2, 3]. As a consequence, most of their properties have been studied in detail and are well understood, at least as far as equilibrium is concerned. In this paper we want to study a new effect which, to our knowledge, has not been considered in the previous literature, although also it has a number of possible applications.

Physically, we ask ourself what is the influence of the solvent on the ability of a polymer to penetrate a porous membrane. If the pores are very big, typically of sizes larger than a collapsed globule but smaller than the Flory diameter of a random coil in a good solvent, the collapse might help in penetrating them. On the other hand, we expect the opposite effect for small pores, typically just slightly larger than a single monomer. In that case a polymer in good solvent can go through a pore by having one monomer pass after the other [4]. For a collapsed polymer this should be less easy, since monomers tend to cluster together. But, as far as we know, no detailed studies of this exist.

Technically, we consider self avoiding walks (SAWs) of N steps on a simple cubic lattice. In a good solvent at temperature $T \to \infty$, the only monomer-monomer interaction is the excluded volume interaction. In a less good solvent, we include an attractive monomer-monomer contact potential which acts between unbonded monomer pairs on nearest neighbour sites on the lattice, and has strength $-\epsilon$, giving for each such contact a Boltzmann factor $q = e^{\epsilon/K_b T}$. The theta point for this model is at $q_\theta = 1.3087 \pm 0.0003$ [5]. The membrane is located in the plane $z = 0$. Its pores are of unit size, and are arranged in checkerboard fashion: sites with even $x+y$ and $z = 0$ are forbidden for the walk, while all other sites are allowed. The walks start at the origin $x = y = z = 0$, i.e. one end is grafted to one of the forbidden sites of the membrane.

We simulate this model using the pruned-enriched Rosenbluth method (PERM) [5]. This is the most efficient known method for simulating theta polymers, but it is also very efficient for conditions not too far from the theta point, including athermal SAWs. For the latter, the pivot algorithm is even more efficient if the SAWs are not constraint by obstacles like our membrane. If there are many such obstacles, PERM becomes more efficient. We have not checked whether the pivot method would be more efficient for the present problem, but this is of little relevance since we were anyhow able to obtain very high statistics data for very long chains ($N = 16000$ at the theta point, $N = 10000$ for athermal SAWs).

To measure how well the polymer can penetrate through the membrane, we use two different "order parameters" (i.e., observables). The first is simply the number N_0 of points on the walk in the plane $z = 0$ (excluding the starting point). For the other, we first define N_+ as the number of monomers in the upper half space $z > 0$, and N_- as the number of monomers at $z < 0$. Obviously, $N_+ + N_- + N_0 = N$. The second order parameter is then

$$\alpha = \frac{2N_+ N_-}{N_+^2 + N_-^2} \ . \qquad (1)$$

In Fig. 1 we plot α against N, for six different values of q. Apart from the strong finite size effects at small N (α vanishes trivially for $N < 4$), there seems to be a power behaviour for $q \leq q_\theta$. Indeed, when plotting $\alpha \sqrt{N}$ against N (Fig. 2), we see that

$$\alpha \sim N^{-1/2} \qquad (2)$$

for theta polymers, while α seems to decrease with a smaller power for polymers in a good solvent. Due to the aforementioned scaling corrections it is hard to give a more precise estimate, our best fit is $\alpha \sim N^{-0.38}$ for SAWs. For collapsed chains α decreases much faster, but it is not clear whether it will finally follow a power law (with power ≥ 1) or whether it falls faster.
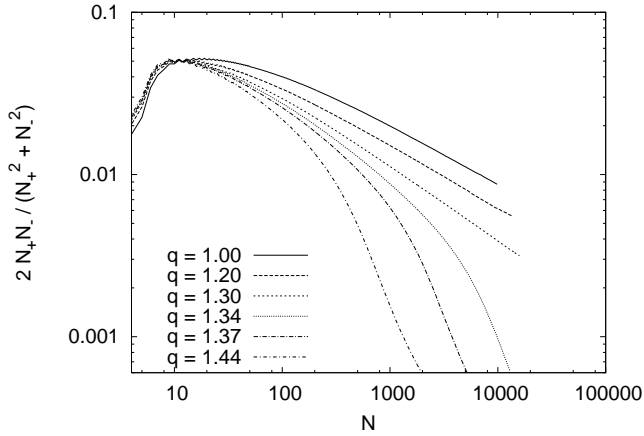
FIG. 1: Log-log plot of α against N, for six different values of q. Data decrease with q. Statistical errors are not larger than the thickness of the lines.

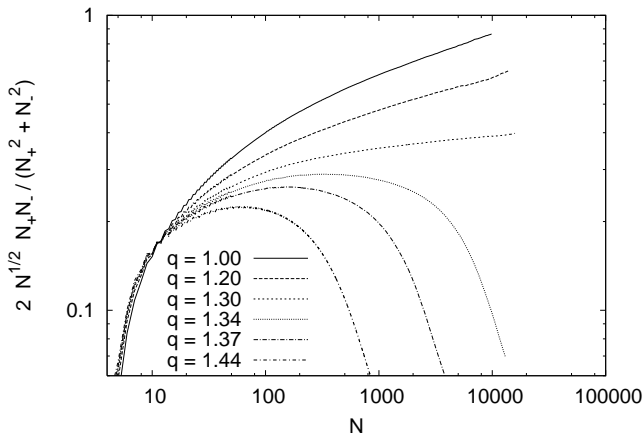

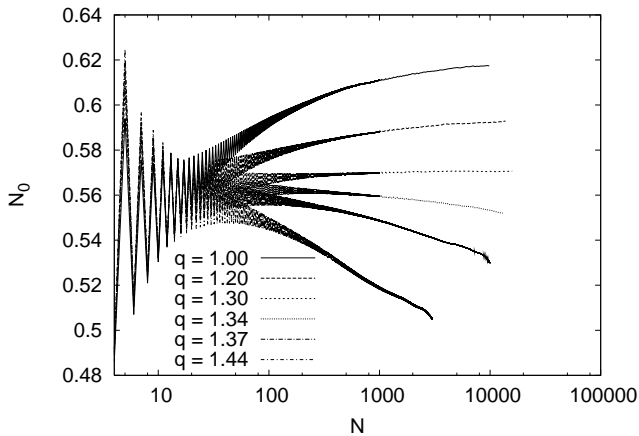FIG. 2: Same data as in Fig. 1, but multiplied by $N^{1/2}$.

FIG. 3: Log-linear plot of $\langle N_0 \rangle$ against N, for the same six different values of q. Again, data decrease with q. The rapid decrease of the data for $q = 1.37$ and $q = 1.44$ at very large N is presumably due to statistical fluctuations.

The average N_0 is plotted against N, for the same six values of q, in Fig. 3. We see huge even/odd oscillations for small N. Apart from that, the results are somewhat complementary to those in Figs. 1 and 2. For $q = q_\theta$ we see that N_0 converges quickly to a constant,

$$N_0 \to 0.5703 \pm 0.0003 \qquad \text{for} \quad N \to \infty \, . \qquad (3)$$

Again scaling corrections are more important for good solvent conditions. But although N_0 keeps increasing with N in this case, it seems to converge nevertheless to a constant. This is definitely no longer true for $q > q_\theta$. There, N_0 seems to converge to zero. We cannot exclude that this happens according to power laws, $N_0 \sim N^{-\beta}$, but then the exponent β would be non-universal, and would increase strongly with q. We consider it much more likely that N_0 decreases, in the collapsed phase, faster than any power of N.

Let us now try to understand these results theoretically, and let us start with $q = q_\theta$. For simplicity we will neglect the logarithmic corrections holding at the theta point [5, 6, 7, 8], and describe the polymers by ideal random walks. In this case, the walks are Markovian. Whenever such a walk arrives at $z = 0$, it will go in the next step to $z > 0$ and $z < 0$ with equal probability, and both possibilities will evolve later in the same way (except for mirror symmetry). Thus, as far as scaling is concerned, this is the same situation as for an impenetrable wall. In this case [9] the monomer density decreases near the wall as z^2, and the number of monomers just touching the wall goes to a constant for $N \to \infty$. This is in agreement with Fig. 3.

The probability that the n-th monomer, with $0 \ll n \ll N$, is at distance z from the wall scales more precisely as $z^2/n^{3/2}$, where the n-dependence is forced by the fact that $\langle z \rangle \sim \sqrt{n}$. Thus the probability that the wall is touched by the n-th monomer scales as $n^{-3/2}$, and this will also be the scaling of the probability that the walk passes through the membrane at "time" n. From this and the Markov property follows immediately Eq.(2).

These simple arguments break down when $q \neq q_\theta$. Now, it does matter that a walk which passes through a pore ends up on the opposite side of the membrane. For $q < q_\theta$ (good solvent conditions) it feels then a weaker excluded volume effect, as compared to the case where it stayed on the same side of the membrane. Thus passing through the membrane is (entropically) favoured, leading to larger values of N_0 and α. On the other hand, passing through the membrane is (energetically) disfavoured for bad solvent conditions, and N_0 and α are reduced in this case. Apart from this very qualitative argument we have not been able to give a more thorough theoretical discussion. For SAWs grafted to a hard wall, the average number of monomers touching the wall goes to a constant for $N \to \infty$ [9, 11]. Thus it is not too surprising that the same holds also when the wall is replaced by a porous membrane, and only monomers within pores are counted. But it is not too obvious either, as the same analogy does not hold for collapsed polymers. While we
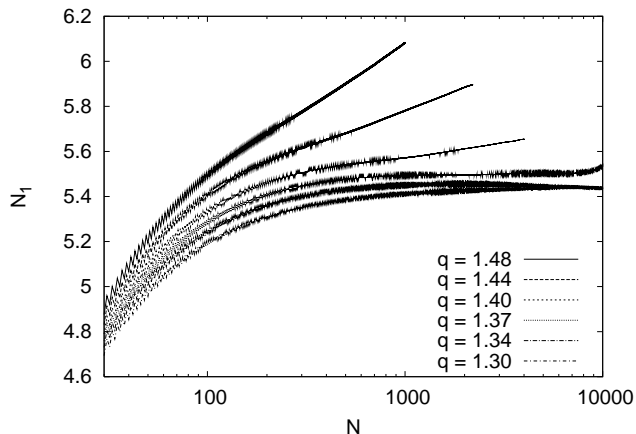
FIG. 4: Number of monomers at distance $z = \pm 1$ from the membrane, N_1, plotted against $\ln N$ for several values of q. While N_1 converges to a constant when $q \leq q_\theta$, it seems to diverge with N for $q > q_\theta$.
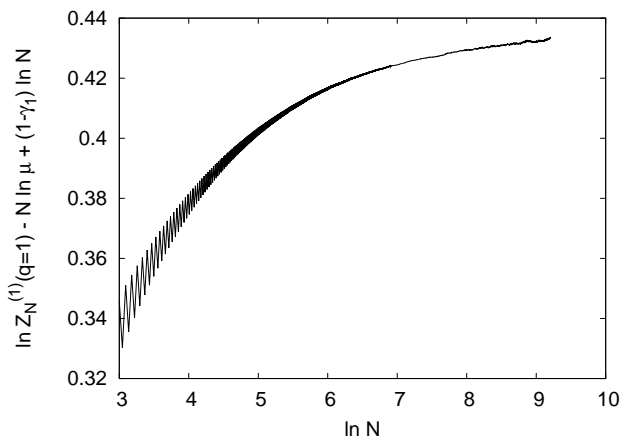

FIG. 5: Logarithm of the partition sum divided by μ^N and multiplied by $N^{1-\gamma_1}$, plotted against $\ln N$. The values used for μ and γ_1 are 4.684038 and 0.679. They were fixed by demanding that the leading corrections to scaling go like $N^{-1/2}$.

found here that N_0 goes to zero for $N \to \infty$, the number N_1 of monomers *touching* the wall or membrane ($z = \pm 1$; here it does not matter whether the membrane has pores or not) diverges with N, when the solvent is bad ($q > q_\theta$; see Fig. 4).

Finally, let us discuss how the porous membrane effects the partition function and the density of states $g(E)$, where $E = -\epsilon m$ with m being the number of monomer-monomer contacts. For SAWs grafted to an impenetrable wall, the partition sum scales as [10]

$$Z_N^{(1)} \sim \mu^N N^{\gamma_1 - 1} \qquad (4)$$

where $\mu = 4.684043(10)$ is the same effective connectivity as for ordinary SAWs, but γ_1 is a modified critical exponent, $\gamma_1 = 0.679(2)$. Numerically (see Fig. 5) we found
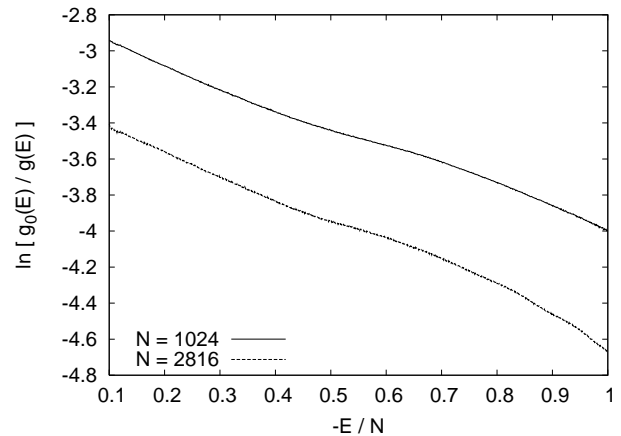

FIG. 6: Ratio between the density of states for polymers grafted to a porous membrane, divided by the analogous density of states for free polymers without a membrane. The logarithm of this ratio is plotted versus $-E/N$, for two different values of N.

that the same ansatz describes also the large N behaviour of athermal SAWs grafted to the porous membrane (in Fig. 5 we used our present best estimates $\gamma_1 = 0.679(1)$ and $\mu = 4.684038(6)$). This is not trivial, since we had just argued that the possibility of penetrating the membrane should increase the partition sum. It does so indeed, but this does not affect the asymptotic behaviour.

Instead of showing the density of states $g(E)$ itself, defined as the number of configurations with energy $-E$, we show in Fig. 6 the ratio $g(E)/g_0(E)$, where $g_0(E)$ refers to polymers in absence of a membrane. More precisely, we plot the logarithm of this ratio against $-E/N$ for two values of N. Here we have assumed that $\epsilon = 1$, i.e. each contact contributes exactly one unit of energy. We see that $g(E)/g_0(E)$ decreases with the absolute value of E, i.e. the effect of the membrane increases with $|E|$. This is of course in agreement with our other measurements. A more careful inspection shows that the curves in Fig. 6 are not straight, but are cup-concave around $E \approx -0.4N$. This means that $g(E)$ is less convex than $g_0(E)$ in the energy range which gives the dominant contributions to the partition sum near the theta collapse, i.e. the theta transition becomes "harder" by the presence of the membrane. For the present model this is a rather weak effect, but is is not inconceivable that it is much stronger in some other microscopic realization. In such a model, grafting polymers to porous membranes may make the collapse transition look first order for intermediate values of N.

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